HYDROGEN PERMEABILITY OF PALLADIUM-COPPER ALLOY COMPOSITE MEMBRANES OVER A WIDE RANGE OF TEMPERATURES AND PRESSURES

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Abstract

The permeability of Pd-Cu alloys containing 40, 53, 60, and 80 wt% Pd has been determined over the 623-1173 K temperature range for H_2 partial pressure differences as great as 2.6 MPa. Pure palladium and copper membranes were also evaluated. Each alloy was evaluated under conditions of fcc structure stability or metastability. The fcc permeability increased steadily with the proportion of palladium, approaching the permeability of pure palladium. The 53wt%Pd-47wt%Cu and 60wt%Pd-40wt%Cu alloys were also evaluated at temperatures within the bcc stability region. For both alloys, the bcc permeability was several times greater than the fcc permeability. However, the 60wt%Pd-40wt%Cu bcc permeability at 623 K was the highest reaching about 70% of the permeability of pure palladium. These bcc alloys were subjected to temperature increases during testing that resulted in transition from bcc to fcc, followed by temperature decreases that should revert the alloys back to bcc. The permeabilities dropped abruptly during the transition from bcc to fcc. On cooling to the bcc stability region, the 60wt%Pd-40wt%Cu alloy slowly regained a bcc permeability while the 53wt%Pd-47wt%Cu did not during the test period. None of the Pd-Cu alloys subjected to testing at 1173 K failed, however all showed some decline in permeability that was attributed to intermetallic diffusion between the membrane alloy and support.

1. Introduction

Hydrogen production is expected to increase in the future as the U. S. moves toward widespread use of hydrogen as an energy carrier. Industrial processes, such as coal gasification, can be used for the production of hydrogen from domestic energy sources, however hydrogen produced in this way is mixed with carbon dioxide and other gases. Advances in membrane technology have the potential to improve the efficiency of hydrogen separation and recovery and reduce the cost associated with hydrogen production. A significant technical barrier impeding hydrogen separation membrane development is their resistance

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to impurities, especially sulfur compounds such as H_2S, that are part of the gasification product gas mixture. Very low concentrations (ppm level) of these sulfur-containing compounds can rapidly and irreversibly deactivate a catalytic metal surface, such as a palladium-based membrane [1-4]. Consequently, the identification of sulfur tolerant membrane compositions and the understanding of the mechanism of sulfur poisoning of hydrogen membranes is critical to this technology. Resistance to sulfur poisoning upon exposure to methyl disulfide has been reported for thin Pd films formed within the macropores of an alumina support [5] and the application of sub-micron films of Pt on Pd has been suggested to enhance sulfur resistance of hydrogen membranes [2, 6-8]. The most promising investigations of sulfur-resistant hydrogen membranes, however, have focused on the use of Pd alloys, especially Pd-Cu alloys. Pd-Cu alloys have exhibited resistance to sulfur poisoning upon exposure to H_2-rich retentate streams containing H_2S at levels of up to 5 ppm [9], 1000 ppm [10] and (at temperatures greater than 773 K) intermittent exposure to 100,000 ppm [7]. Permeability has been evaluated with H_2S in the hydrogen retentate stream [9, 10] and with sulfur-free retentate streams [9-16].

The highest reported values of Pd-Cu alloy permeability were comparable to the permeability of pure Pd and occurred for a composition of 60wt%Pd-40wt%Cu [9,11,13,17]. High permeability values at this particular composition are attributable to the high mobility of hydrogen atoms within the body-centered-cubic (bcc) crystal structure (β phase) of the Pd-Cu alloy [18-21] relative to the face-centered cubic (fcc) continuous solid solution (α phase), Figure 1. Attempts to make Pd-Cu alloy membranes more economically viable have focused on the manufacture of ultra-thin Pd-Cu alloys on porous substrates. Way, McCormick and coworkers are investigating the electroless deposition of thin films (1-10 μm) of Pd-Cu alloys on porous ceramic substrates [22,23]. Ma and coworkers have employed electroless deposition techniques to prepare thin films of Pd-Cu alloys on porous stainless steel substrates [24].

Figure 1. Pd-Cu Phase Diagram based on data summarized by Henkel [21]. Numbered points represent permeability measurements discussed below.
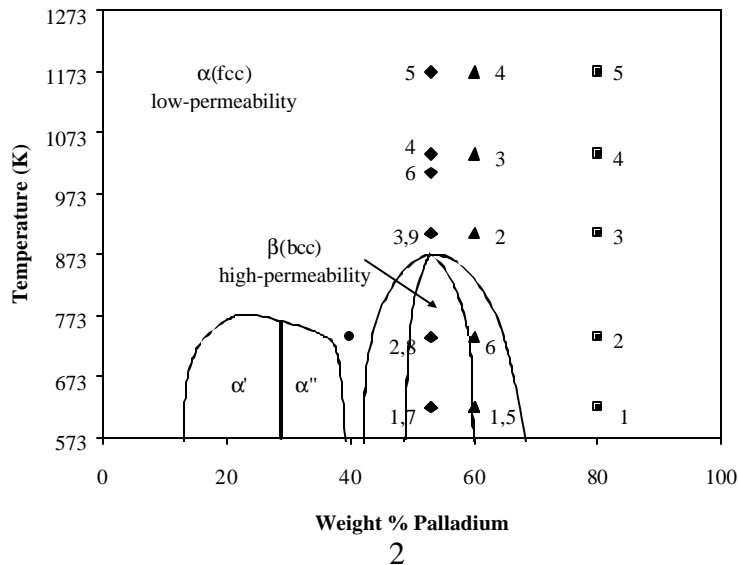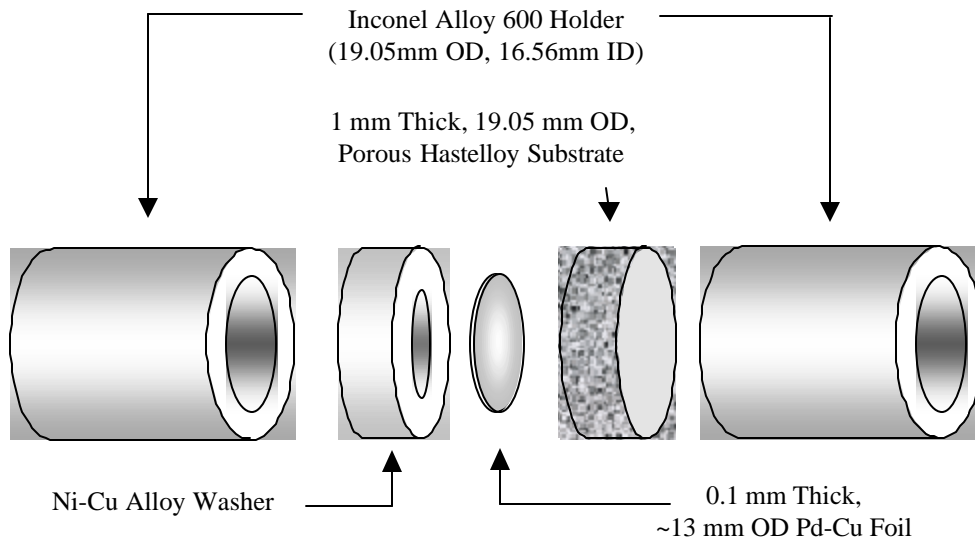
Previous assessments of the permeability of Pd-Cu alloys have typically been determined at low H_2 partial pressure over a limited range of low temperatures, with most data being generated for the 60wt% Pd - 40wt% Cu alloy. The objective of this study was to assess the hydrogen permeability of Pd-Cu alloys over the wide ranges of temperature and pressure associated with conceptual, post-gasifier, water-gas shift membrane reactors and to correlate the measured permeabilities with membrane alloy crystal structure. Four Pd-Cu alloys were selected, 40%Pd-60%Cu (a composition outside of the bcc phase region on the low Pd side), 53%Pd-47%Cu (the composition in the middle of the bcc phase region), 60% Pd-40%Cu (the composition most commonly cited as yielding the greatest H_2 permeability) and 80%Pd-20%Cu (a composition far removed from the bcc phase region and intermediate to the 60%Pd-40%Cu alloy and pure Pd). The permeability values of pure palladium and pure copper membranes were also included in this evaluation.

2. Experimental Details

Palladium-copper alloy foils, 99.9% purity, 0.1 mm (100 µm) thick, were prepared by ACI Alloys, San Jose, California. Palladium foil, 99.9%, 0.1 mm thick, and copper foil, 1.0 mm thick, were obtained from Alfa Aesar. Membranes were fabricated for testing by brazing foil disks to thick nickel alloy washers having negligible hydrogen permeability using high-purity gold powder. Brazing was done in a muffle furnace at 1400 K. A porous metal support was utilized on the permeate side of the membrane foil to prevent foil distortion and possible mechanical failure at high temperatures in the presence of a pressure drop. The membrane surface contacted the porous support surface but was not bonded to it. The resulting mounted membranes, shown in an exploded view in Figure 2, had an active hydrogen permeation diameter of 8.5 mm. The membrane brazing and mounting techniques were developed at the National Energy Technology Laboratory (NETL).

Figure 2. Schematic of the palladium/copper alloy membrane assembly.

Inconel Alloy 600 Holder
(19.05mm OD, 16.56mm ID)

1 mm Thick, 19.05 mm OD,
Porous Hastelloy Substrate

Ni-Cu Alloy Washer

0.1 mm Thick,
~13 mm OD Pd-Cu Foil

Some membranes were annealed for crystal structure control following mounting. Annealing was done by placing the mounted membrane in a tube furnace at a selected temperature under flowing nitrogen. The membrane was held at temperature for a period of time, quenched and characterized.

The hydrogen membrane test (HMT) unit, fabricated at the NETL, was designed to evaluate membrane performance at high-pressures and temperatures via steady-state hydrogen flux testing and has been described previously [25]. The apparatus was designed to operate at temperatures and pressures of up to 1173 K and 3 MPa, respectively. A schematic of the apparatus is shown in Figure 3, which illustrates the gas flow pathways. A 90% H_2-10% He mixture was fed to the unit on the retentate side and ultra-high purity Ar sweep gas was supplied to the permeate side. Flow rates were controlled such that the concentration of hydrogen in the permeate did not exceed 4.0 mol%. Although the HMT unit has the capability of operating at total pressure differentials in excess of 3.0 MPa, the sweep gas pressure was adjusted to maintain a small total pressure gradient of 0.14 MPa, though the hydrogen partial pressure gradient remained as high as 2.6 MPa.

Figure 3. Schematic of NETL's Hydrogen Membrane Testing (HMT) unit.
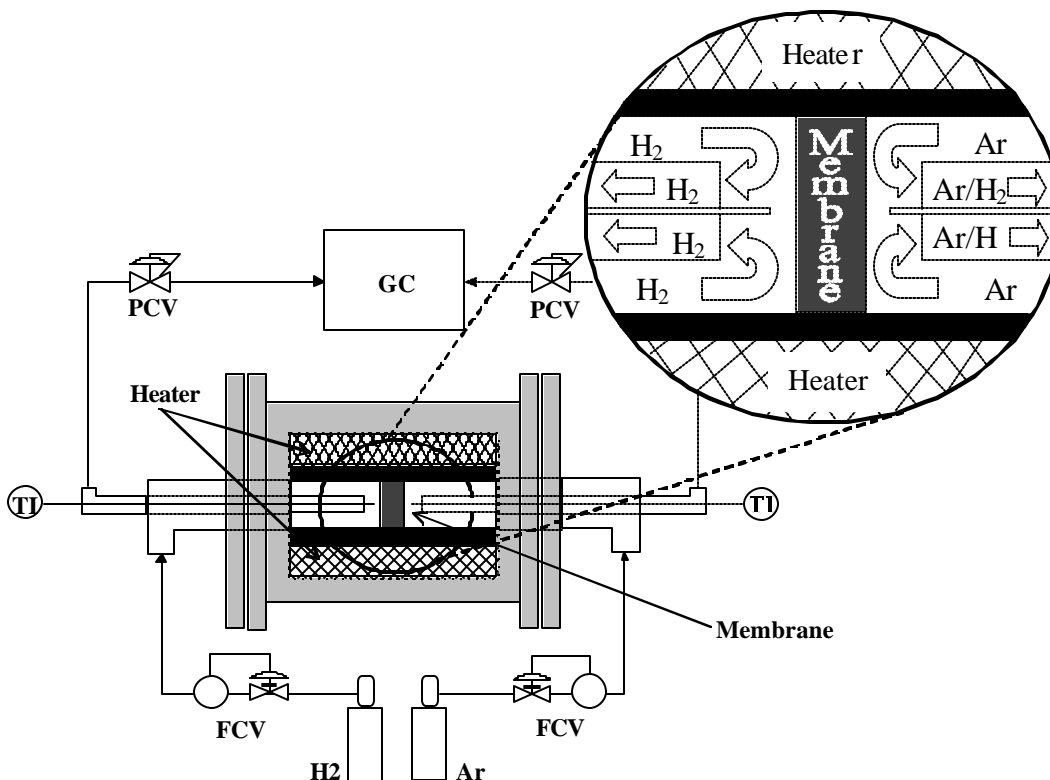
Membranes were characterized prior to and after permeability testing. Membranes were recovered following testing by cutting them out of the extension tubes using a small, dry abrasive blade taking care to control contamination. To

allow characterization of the permeate surface of the used membranes, the support was removed by carefully hand-cutting the welded seam. The membrane surfaces were photographed and examined through a stereomicroscope. Characterization techniques included x-ray diffraction (XRD) and scanning electron microscopy (backscattered mode) with energy dispersive spectroscopy (SEM/EDS).

3. Results and Discussion

The flux of hydrogen through each membrane was proportional to the difference of the square root of the hydrogen partial pressures on the retentate and permeate sides of the membrane. Thus, Equations 1 and 2 were used to represent the performance of the membrane in terms of permeability, k, and permeance, k', respectively.

$$N_{H2} = -k \frac{\left(P_{H2,ret}^{0.5} - P_{H2,perm}^{0.5} \right)}{X_M} \qquad\qquad 1$$

$$N_{H2} = -k' \left(P_{H2,ret}^{0.5} - P_{H2,perm}^{0.5} \right) \qquad\qquad 2$$

In both expressions, N_{H2} represents the flux of H_2, $P_{H2,perm}$ represents the hydrogen partial pressure in the permeate, and $P_{H2,ret}$ represents the hydrogen partial pressure in the retentate.

Permeability results for the 53%Pd-47%Cu and 60%Pd-40%Cu membranes are presented in Figures 4 and 5 and the permeability results for both 40%Pd-60%Cu and 80%Pd-20%Cu membranes are presented in Figure 6, all as a function of inverse absolute temperature. The Pd-Cu alloys were completely selective for hydrogen. The number associated with each data point in Figure 1 corresponds to the sequential order of the membrane's temperature history. The permeability values of Pd and Cu are also included in Figure 4, 5 and 6 for comparison. The data point number for each permeability value is referred to parenthetically in the following discussion. Table 1 summarizes the alloy phase structure determined by XRD measurement at ambient temperature and the structure expected based on the phase diagram [21].

The 53%Pd-47%Cu alloy permeance was initially measured at 623 K (1) and then at 738 K (2), Figure 4. This alloy composition corresponds to the middle of the bcc region shown in Figure 1, which has a bcc to fcc transition temperature of 871 K. Therefore these permeance values (1) and (2) corresponded to the bcc structure. Nonetheless they were more than an order-of-magnitude less than that of pure Pd. XRD results verified that this membrane was bcc as loaded into the reactor. When the membrane was heated beyond 871 K to 908 K (3), the permeance diminished because of the temperature-induced transition of the bcc structure to the less permeable fcc structure. The membrane exhibited fcc permeance values as the membrane was heated to higher temperatures of 1038 K (4) and 1173 K (5), and then cooled to 1008 K (6) and 623 K (7) before being

heated again to 738 K (8) and 908 K (9). Based on the observed flux response, the membrane retained the fcc structure when cooled to 623 K (7). Even after approximately 110 hours of flux testing at 623 K (7), the alloy showed no evidence of transforming back to bcc. The membrane was not permitted to remain at 623 K for an extended period of time, however, to determine if it would ultimately revert to the bcc phase. Also, no evidence was observed in the permeation behavior at 738 K (8) and 908 K (9) that suggested a phase transformation to bcc.

The permeability of the 60%Pd-40%Cu alloy, Figure 5, diminished when temperature increased above about 840 K (the temperature at which the bcc to fcc transition occurs as shown in Figure 1) to 908 K (2). The membrane was then heated to 1038 K (3) and 1173 K (4) prior to being cooled to 623 K (5). These permeability values (2,3,4,5) were well correlated by an Arrhenius type equation and corresponded to fcc phase permeability values that were about one-tenth that of pure Pd. As the membrane was heated to 738 K and maintained at this temperature for 74 hours (6) the permeability increased to a value greater than that indicated by the line correlating the results of conditions (2,3,4,5). The membrane was then cooled to 623 K (7) and maintained at this temperature for 22 hours. The permeability (7) was greater than that observed at condition (5) but less than that of the first measurement at this temperature (1). The elevated permeability values associated with conditions (6) and (7) indicate that the membrane structure was slowly reverting to bcc because the temperature was being maintained at values less than 840 K for an extended period of time.

Table 1. Phase composition of Pd-Cu alloy membranes.

Composition (Pd:Cu, wt%)	Preparation Method	Membrane Phase* (determined by XRD)	Expected phase (from Figure 1)
80:20	Brazed 1400 K, 4 min, then cooled to ambient over about 5 min.	fcc	fcc
60:40	As brazed	fcc	bcc
	Annealed, 588 K, 66h, under nitrogen	bcc	bcc
60:40 second preparation	As brazed	Mixed fcc - bcc	bcc
53:47	As brazed	bcc	bcc
40:60	As brazed	fcc	fcc

* Alloy phase determined at ambient temperature and represents phase present when membrane was loaded into reactor.

Figure 4. Permeability of the 53wt%Pd-47wt%Cu Alloy as a function of temperature and history; 1 = First Condition, 9 = Last Condition.
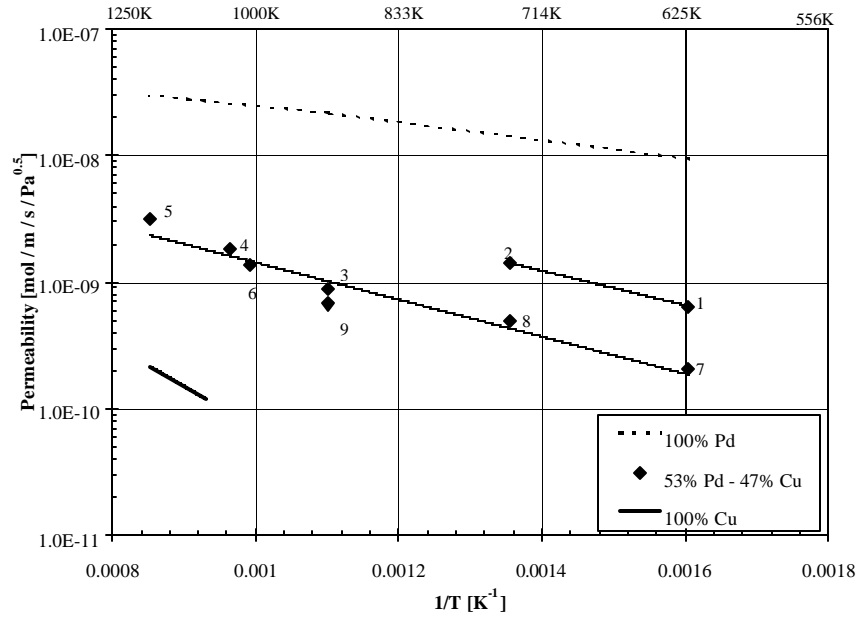

Figure 5. Permeability of the 60wt%Pd-40wt%Cu alloy as a function of temperature and history; 1 = First Condition, 7 = Last Condition.
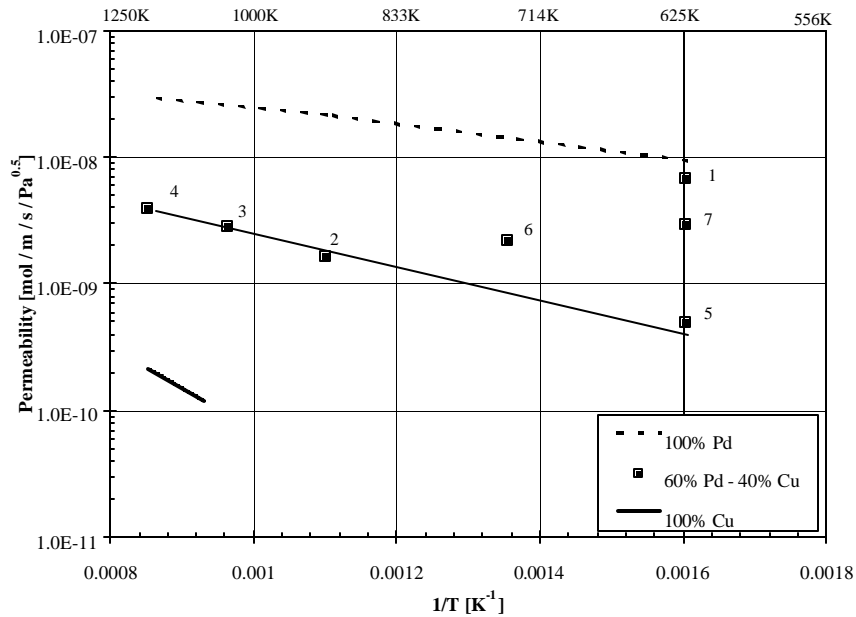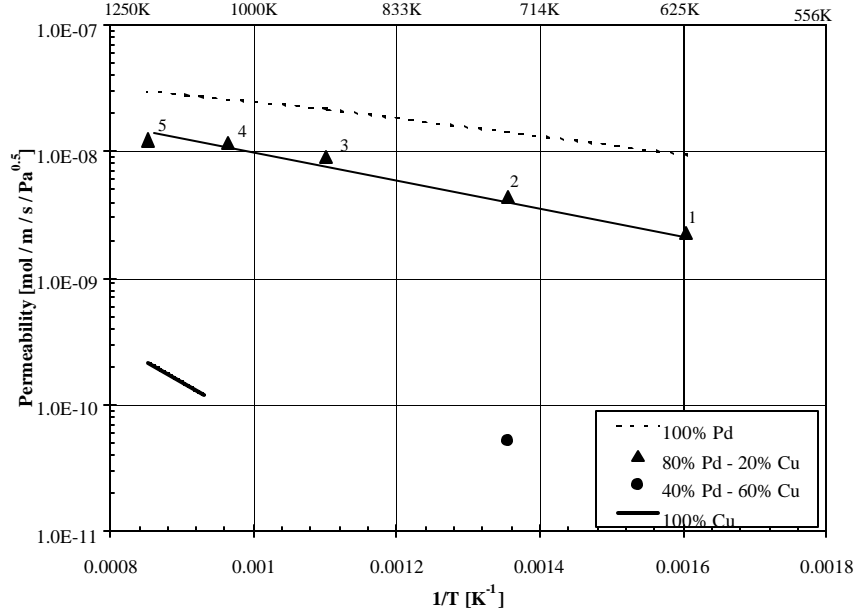
Figure 6. Permeability of the 80wt%Pd-20wt%Cu and 40wt%Pd-60wt%Cu alloys as a function of temperature. For 80wt%Pd-20wt%Cu the temperature history is represented by 1 = First Condition to 5 = Last Condition.


According to the phase diagram in Figure 1, the 80%Pd-20%Cu alloy should be fcc over the entire temperature range examined. This alloy exhibited permeability values of roughly 30% of pure Pd over the 623–1173 K temperature range, as shown in Figure 6. Although the 80%Pd-20%Cu alloy was less permeable than the 60%Pd-40%Cu alloy at 623 K, an Arrhenius correlation fit all of the permeability values. The 80%Pd-20%Cu alloy exhibited higher permeability values than the 53%Pd-47%Cu alloy at all temperatures, while it exceeded the permeability of the 60%Pd-40%Cu alloy at temperatures greater than 840 K.

The 40%Pd-60%Cu alloy should also be fcc over the entire temperature range examined according to the phase diagram although an updated phase diagram [20] suggests a more complicated phase behavior at temperatures below about 698 K. This phase region is not expected to impact the test results for this composition since the flux below 698 K was not detectable. The permeability at 738 K, Figure 6, was very low, about one thousandth that of Pd. Since this alloy composition is expected to be fcc over the temperature range 738 to 1173 K, the permeability is expected to remain very low. As of the preparation of this manuscript, data is still in the process of being collected on this alloy so the permeability behavior over the full temperature-pressure range is not yet known.

Most of the membranes examined in this study exhibited some decline in permeability when held at 1173 K for an extended period of time. This decline was most pronounced for the 80%Pd-20%Cu alloy, Figure 6, which showed a permeability decline of about 0.5% per hour at 1173 K. This membrane was

separated from the support for examination after flux testing. During the separation procedure, it was noted that the membrane foil had adhered to the porous support. SEM/EDS analysis showed that the membrane foils had fused to the porous support as indicated by distorted areas where the foils and support had been ripped apart. Examples of this adhesion are shown in Figure 7. EDS of these contact points showed that Hastelloy fragments remained attached to the foil. In addition, EDS analysis of membrane foil areas away from these contact points provided evidence of significant intermetallic diffusion. Ni, Cr and Fe, major components of Hastelloy, were detected in all areas examined. This membrane-support interaction was observed in all membranes examined following testing at 1173 K and is likely the cause of the observed permeability decline at 1173 K. This permeability decline is possibly due to both membrane area loss and crystal structure effects from the intermetallic diffusion. This intermetallic diffusion could also be responsible for the failure of the 53%Pd-47%Cu alloy to convert to the bcc structure on cooling into the bcc stable region during testing as noted above.

Figure 7. SEM images illustrating adhesion points and damage to the membrane surface.

Adhesion points   Membrane surface   Porous support
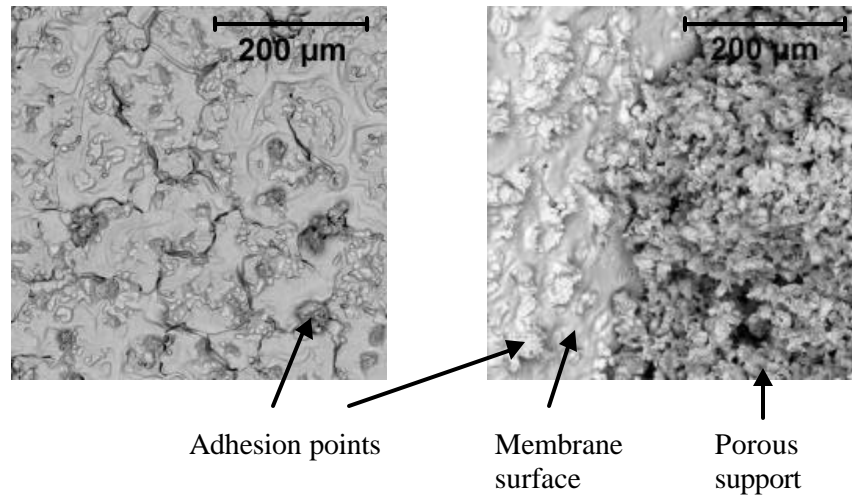
4. Conclusions

Pd-Cu alloys exhibit hydrogen permeability values intermediate to palladium and copper over the 623-1173 K temperature range and 0.1 – 2.6 MPa pressure range. The 53%Pd and 60%Pd alloys exhibited relatively high permeability values at temperatures corresponding to bcc crystal structure. Although the 53%Pd alloy exhibited bcc permeability values over a wider range of temperature, the 60%Pd alloy exhibited the highest permeability value (relative to pure Pd) after equilibration at 623 K. The permeability of the 60%Pd alloy dropped markedly at temperatures greater than 850 K due to the transition of the Pd-Cu crystal structure from bcc to fcc. The 60%Pd membrane retained low permeability values when initially cooled to temperatures below 850 K, but the alloy slowly increased in permeability as the membrane was maintained at 623 K due to the

slow conversion from fcc to bcc structure. Conversely, the 53%Pd alloy retained a low fcc permeability even after extended time at temperatures below the fcc-bcc conversion temperature. Although the permeability of the 80%Pd alloy was less than that of the 60%Pd alloy at 623 K, the 80%Pd alloy exhibited greater permeability values at temperatures greater than or equal to738 K. At 1173 K a slow decline in permeability was noted for all Pd-Cu alloy membranes. This decline was attributed to intermetallic diffusion between the membrane and the support and/or surface blocking. Future work will be directed at determining the temperature and composition range (and corresponding crystal structure) over which various Pd-Cu alloys exhibit resistance to sulfur poisoning as well as the surface chemistry of any poisoning resistance.

Acknowledgement and Disclaimer

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